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Title: Experimental and Modeling Studies of the Exchange Current at the Alkali Beta"-Alumina / Porous Electrode / Alkali Metal Vapor Three Phase Boundary

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The microscopic mechanism of the alkali ion - electron recombination reaction at the three phase boundary zone formed by a porous metal electrode in alkali vapor on the surface of an alkali β''-alumina solid electrolyte (BASE) ceramic has been studied by comparison of the expected rates for the three simplest reaction mechanisms with known temperature dependent rate data; and the physical parameters of typical porous metal electrode/BASE/alkali metal vapor reaction zones. The three simplest reactions are tunnelling of electrons from the alkali coated electrode to a surface bound alkali metal ion; emission of an electron from the electrode with subsequent capture by a surface bound alkali metal ion; and thermal emission of an alkali cation from the BASE and its capture on the porous metal electrode surface where it may recombine with an electron. Only the first reaction adequately accounts for both the high observed rate and its temperature dependence. New results include crude modeling of simple, one step, three phase, solid/solid/gas electrochemical reaction.

Experimental and Modeling Studies of the Exchange Current at the Alkali Beta''-Alumina / Porous Electrode / Alkali Metal Vapor Three Phase Boundary

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The microscopic mechanism of the alkali ion-electron reaction at the three phase boundary zone formed by a porous metal electrode in alkali vapor on the surface of an alkali β''-alumina solid electrolyte (BASE) ceramic in AMTEC cells has been studied by comparison of the expected rates for the three simplest mechanisms with known temperature dependent rate data, using physical parameters of porous metal electrode/BASE/alkali metal vapor reaction zones. The three simplest reactions are tunnelling of electrons from the electrode to a surface bound alkali metal ion; emission of an electron from the electrode with subsequent capture by a surface bound alkali metal ion; and thermal emission of an alkali cation from the BASE, with capture on the metal surface with reduction. Only the first reaction adequately accounts for the high observed rate and its temperature dependence. [1-4]

The interfacial reaction rate is only activated to the degree that the reactant activities are activated, and if it can be explained by a reaction zone near the 3-phase boundary, the likely mechanism is electron tunnelling from the electrode to a Na^+ ion at the surface of the beta''-alumina. This requires tunnelling through a barrier equal to the work function of the electrode surface (~2.5eV) with a barrier thickness of ≤ 1.0 nm. The alkali atoms produced on the BASE surface and will desorb readily at temperatures (> 700K) studied. Measurements performed on mature thin (0.5μm) Mo and (1.0-1.5μm) W/Rh and W/Pt electrodes give consistent exchange currents which are proportional to collision rates of Na gas at the interface over several hundred K.[1,2] The transfer coefficient, a, is always determined to be close to 0.5 for high quality impedance data on mature electrodes at high temperatures, T> 1100K.[2] This argues for a simple, one-step, symmetric reaction for $Na^+ + e^- \rightarrow Na$. The exchange currents of the thin Mo electrodes decrease somewhat over several hundred hours at about 1200K as the grain size increases, and the $Mo/BASE/Na_G$ contact zone decreases in magnitude.[3] For high performance Mo electrodes, using data for grain sire, void area, and approximate electrode grain/BASE contact angle, the length of the three-phase boundary, is estimated to be 3-6 x 10^4 cm per cm^2 of projected geometric electrode area. At zero net current flow, one out of each 500 to 2000' collisions which occur results in a reaction to produce sodium ions in the BASE and electrons in the porous metal electrode. If the entire three phase zone were electrochemically active, it would need to be only ~0.5nm wide. This may not be too great a rate to be caused by simple collisions and electron tunneling near the three-phase boundary. The reaction probability, P, for electron tunneling to a sodium ion at distance a in a defect plane edge is described using as a model a simple rectangular potential barrier with a height equal to the electrode's work function, ϕ ≈ 2.5 eV$=4.00 \times 10^{-19}$ J, for a Mo or W alloy electrode covered with a partial monolayer of Na; The electron's energy is E_e; and the total barrier height is $V = E_e + \phi$. The electron mass is $m_e = 9.11 \times 10^{-31}$ kg; and Planck's constant h$=6.626 \times 10^{-34}$ J-s. The probability P is given in Eq.1a: [5]

. $P \approx 16E_c(V-E_c)V^{-2} \exp[-4\pi a(2m_e\phi)^{1/2}/h]$ (Eq.1a)

For T= lOOOK, the tunnelling electron's energy is $E_c \approx kT = 1.38\times10^{-20}$ J, where k= 1.381×10^{-23} J/K is Boltzmann's constant; and $V = E_c + \phi \approx 4.14\times10^{-19}$ J.

$P \approx 0.515(\exp[-4\pi a(2m_e\phi)^{1/2}/h])$ (Eq.1b)

The tunnelling probability at a = 0.5nm is P = 1.7x104, and the probability decreases rapidly away from the electrode. The tunneling probability is" consistent with the reactant/product densities and the observed lack of significant activation energy strongly support this mechanism and suggests the BASE defect block edge as the reaction site, and indicates that the reaction occurs quite close (< lnm) to the three phase boundary. Calculation of a reaction rate from Eq. la requires estimates of the densities of initial and final states, and the attempt frequency. The value of the reaction rate is taken to be the product of the surface concentration of Na^+; an absolute attempt frequency equal to kT/h; and the transmission probability, P, given above. [6]

$k = d(Na^+) \times (kT/h) \times (.515(\exp[-4\pi a(2m_e\phi)^{1/2}/h]))$ (Eq.2)

where $d(Na^+)$ is the density of accessible Na + ions at a distance a from the emitting electrode surface, where the density of electrons of appropriate energy capable of tunneling is d(e). At 1000K, kT/h is equal to 2.084×10^{13} s^{-1}. A circulation for a =.4 to .6 nm gives contributions to the reaction rate of k= .14 to 3.5×10^{U} atoms/m^2, equivalent to j = .23 to S.6x10^{5}Amps/m^2. These calculations show that observed exchange currents in real electrodes, typically about 1×10^5 Amps/m^2, arc quite consistent with calculations of the reaction rates and exchange currents based on known, if imprecise, electrode and electrolyte properties.

      A somewhat fuzzy experimental upper limit on the extent of the reaction zone can also be established, since the sintering of thin Mo electrodes at -1200K leads eventually to a drop in the observed exchange current after the Mo grain size has reached approximately 0.6 to 1.0 μm and holes in the Mo film of 1.0 to S.0 μm appear.[4] Therefore we can expect that the upper limit of the extent of the reaction zone is less than 1.0 μm and the lower limit is on the order of about 1.0 nm. The upper limit distances are beyond the expected range of electron tunneling, although a hopping mechanism could be used to explain a long range e^-/Na^+/Na reaction if it is ever observed. Further support for the short reaction zone comes from the observation of exchange currents in $Mo/Na_2MoO_4/Na_2Mo_3O_6$ which are 5 to 6 times higher than in oxide free Mo electrodes. In $Mo/Na_2MoO_4/Na_2Mo_3O_6$ electrodes, a mixture of ionic and electronically conducting phases covers the BASE surface, increasing the effective reaction zone area significantly. [4]

      Other potential mechanisms involve thermionic emission of electrons from the metal surface followed by Na^+ ion capture of electrons which "stick" to the BASE surface; or Na^+ ion evaporation from the BASE surface to the metal. Gas phase reaction of Na $^+$ ions with electrons supplied by thermionic emission or tunnelling can only be important if Na^+ ion evaporation has a high rate. The Richardson equation for thermionic emission is:[7]

$j_c = AT\exp(-\phi/kT)$ (Eq.3)

A is a constant and j_c is the emission current in Amp/cm^2.The value of the exponential term at 1000K is 2.6×10^{13}, so that unless A is exceedingly large, thermionic emission,. while not completely negligible in magnitude, would give rise to a electrochemical rate which would be strongly activated, and smaller in magnitude than tunneling.

      The rate, or flux, of escape of Na^+ ions from the active fraction, F_{RCT}, of the BASE surface, k_{Na+}, or j_{Na+}, will be a highly activated process, and the density of Na^+ ions above BASE at about lOOOK will be low.

$k_{Na+} \leq (F_{RCT})[d(Na^+)](kT/h)[\exp(-E_1/kT)]$ (Eq.4)

. The 'first two terms in this expression give the total number of Na^+ ions on the BASE surface; the third term is the absolute evaporation attempt frequency at T= 1000K.[6] The exponential gives the probability of the energy of Na^+ ions necessary for vaporization from the BASE surface, $E_I \approx 2.64eV$, which is approximately the ionization potential of a free Na atom, $1P = 5.139$ eV, minus the work function, $\phi \approx 2.5eV$. The ion evaporation step is highly thermally activated. In spite of the favorable supply of Na^+ ions on the BASE surface, this mechanism requires a much stronger temperature dependence than found for the exchange currents observed at AMTEC electrode.

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